



# The impact of the Tennessee Valley Authority (TVA) coal ash spill on the quality of the Emory and Clinch Rivers: the first year evaluation

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## Introduction:

On Monday, December 22, 2008, the containment structure surrounding the storage of coal ash at the Kingston coal-burning power plant of Tennessee Valley Authority (TVA) collapsed, which resulted in massive release of coal combustion products (CCP) to the environment near Harriman, Tennessee. The CCP material, consisting of fly ash and bottom ash, spilled into tributaries of the Emory River and directly into the Emory River, which joins the Clinch River and flows to the Tennessee River, a major drinking water source for downstream users. The Kingston coal ash spill released over 4.1 million cubic meters of ash, which is one of the largest spills in U.S. history.

A year-long systematic monitoring of the of the environmental impacts of the coal ash spill at the TVA Kingston coal fired power plant has revealed that interaction of the coal combustion products (CCPs) with natural waters mobilizes leachable coal ash contaminants (LCACs) such as boron, arsenic, selenium, strontium, and barium (Ruhl et al, 2009). Since January 2009 we have monitored the quality of water and sediments in downstream segments of the Emory and Clinch Rivers near the spill site. This paper aims to provide an assessment of the potential environmental impacts and remediation activities associated with the Kingston TVA coal ash spill by monitoring the water quality of the Emory and Clinch rivers and testing the boron isotopes as potential proxies for identification of coal ash contamination.

## Analytical Methods:

Coal ash, sediments from the rivers, and water samples from tributaries, the Emory and Clinch Rivers, and springs near the spill area in Kingston and Harriman, TN (Figure 1) were collected in six field trips in 2009. The surface water samples were collected near the river shoreline and in different locations and depths in the river at sites located upstream and (at different distances) from the ash spill.

- Trace metals in water were measured by inductively coupled plasma mass spectrometry (ICP-MS);
- Cations were measured by direct current plasma spectrometer (DCP).
- Anions were measured by an ion chromatograph (IC);
- Boron and strontium isotopes were measured in a thermal ionization mass spectrometer (TIMS).

## Samples Collected:

Sample	# of samples
Porewater	15 samples in 3 trips
Surface water	~130 samples in 9 trips

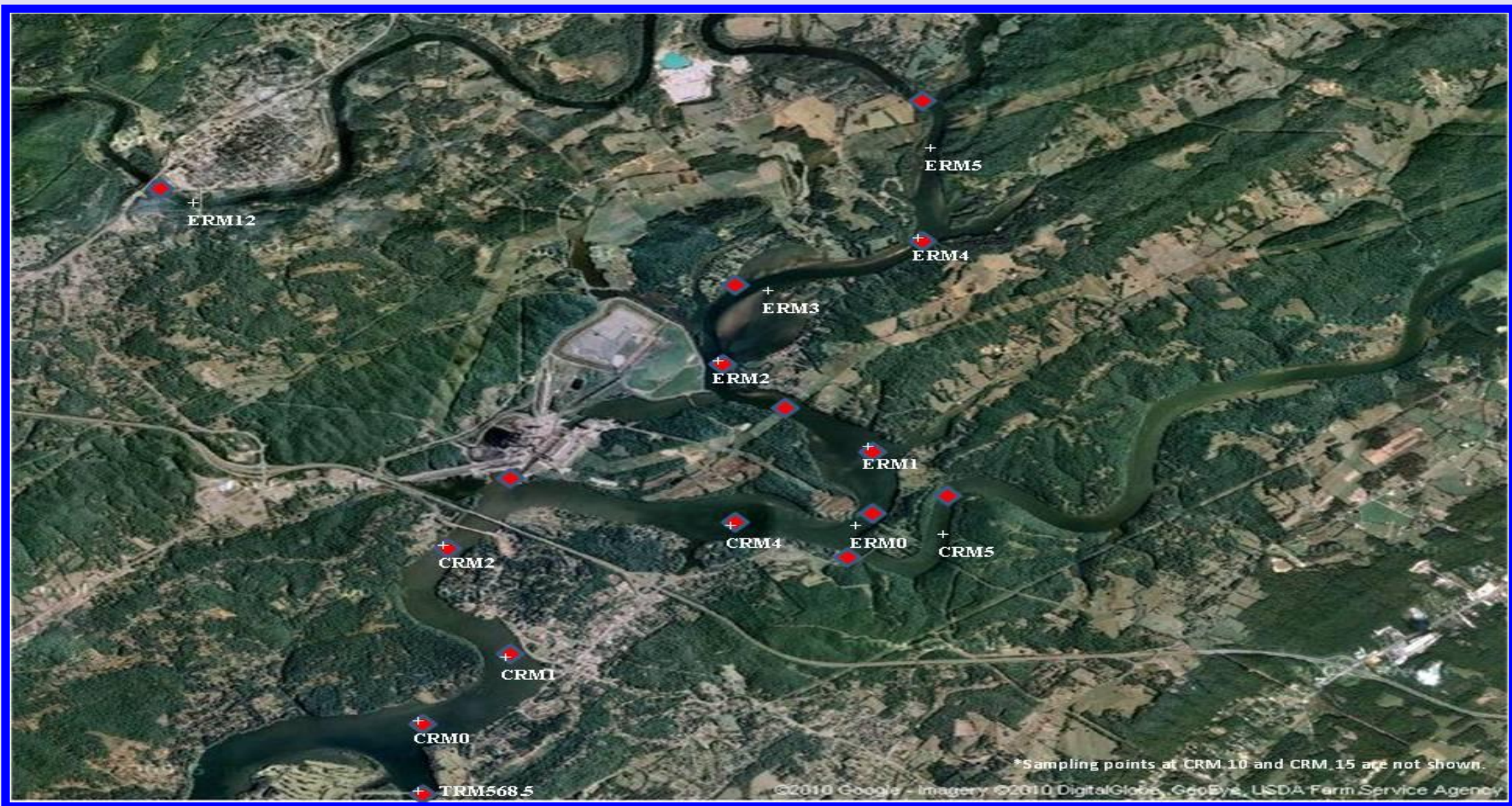


Figure 1: Map of spill region and Duke Sampling locations (red diamonds)

## Results:

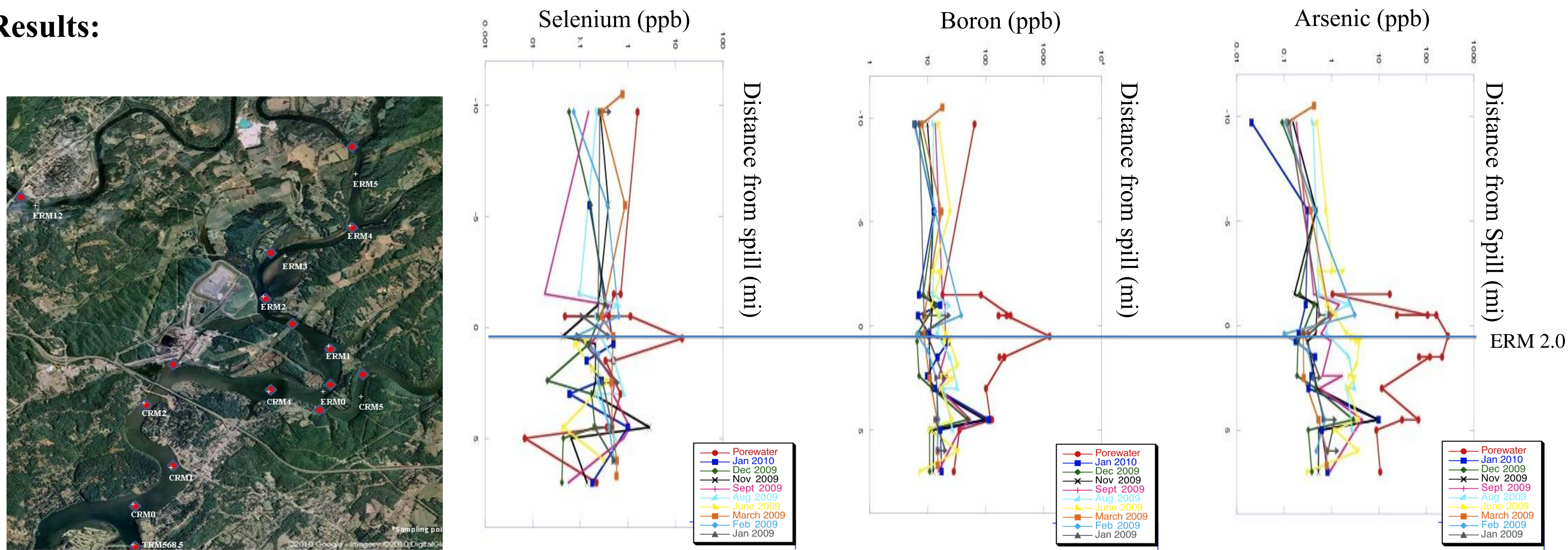
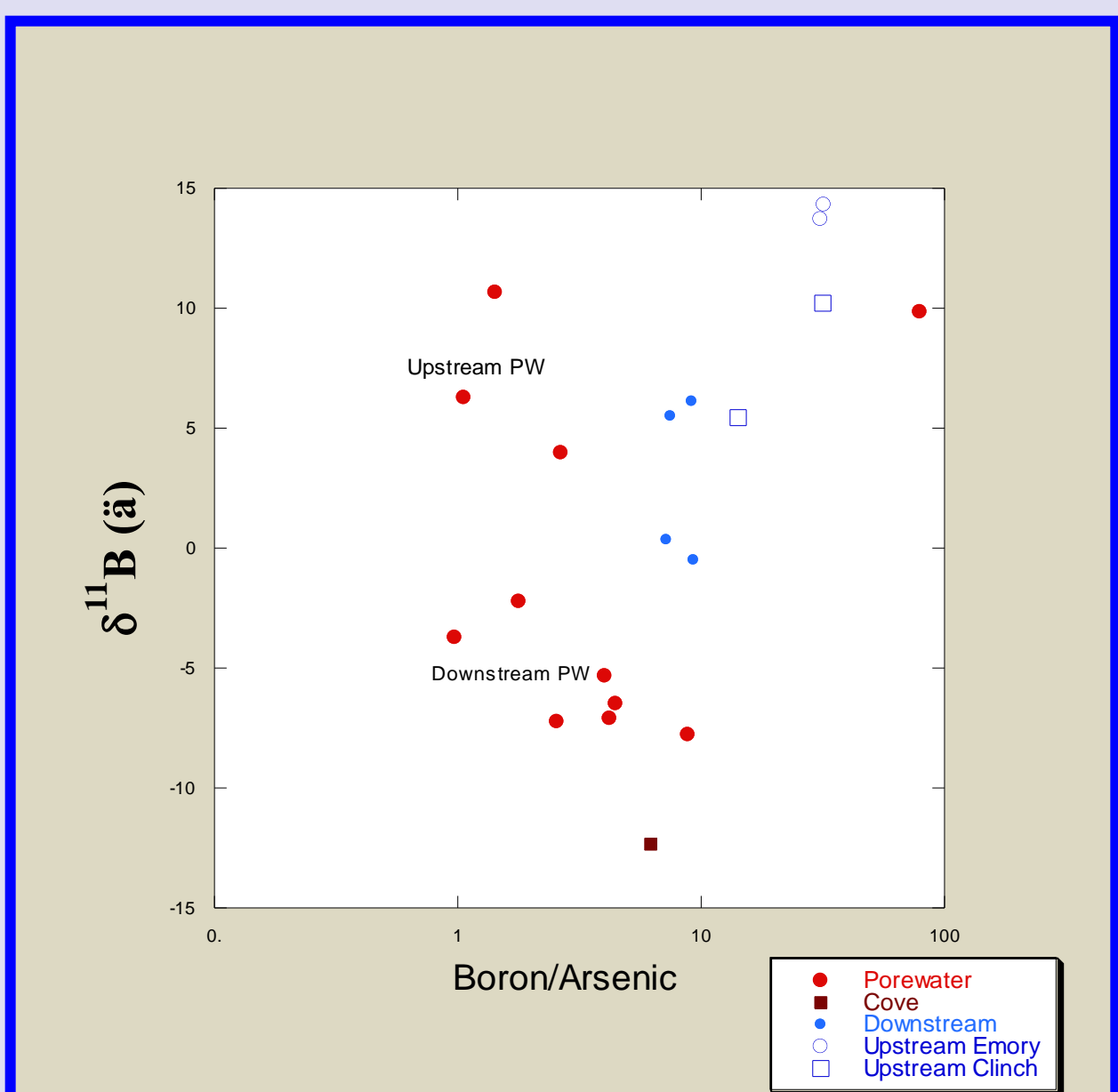
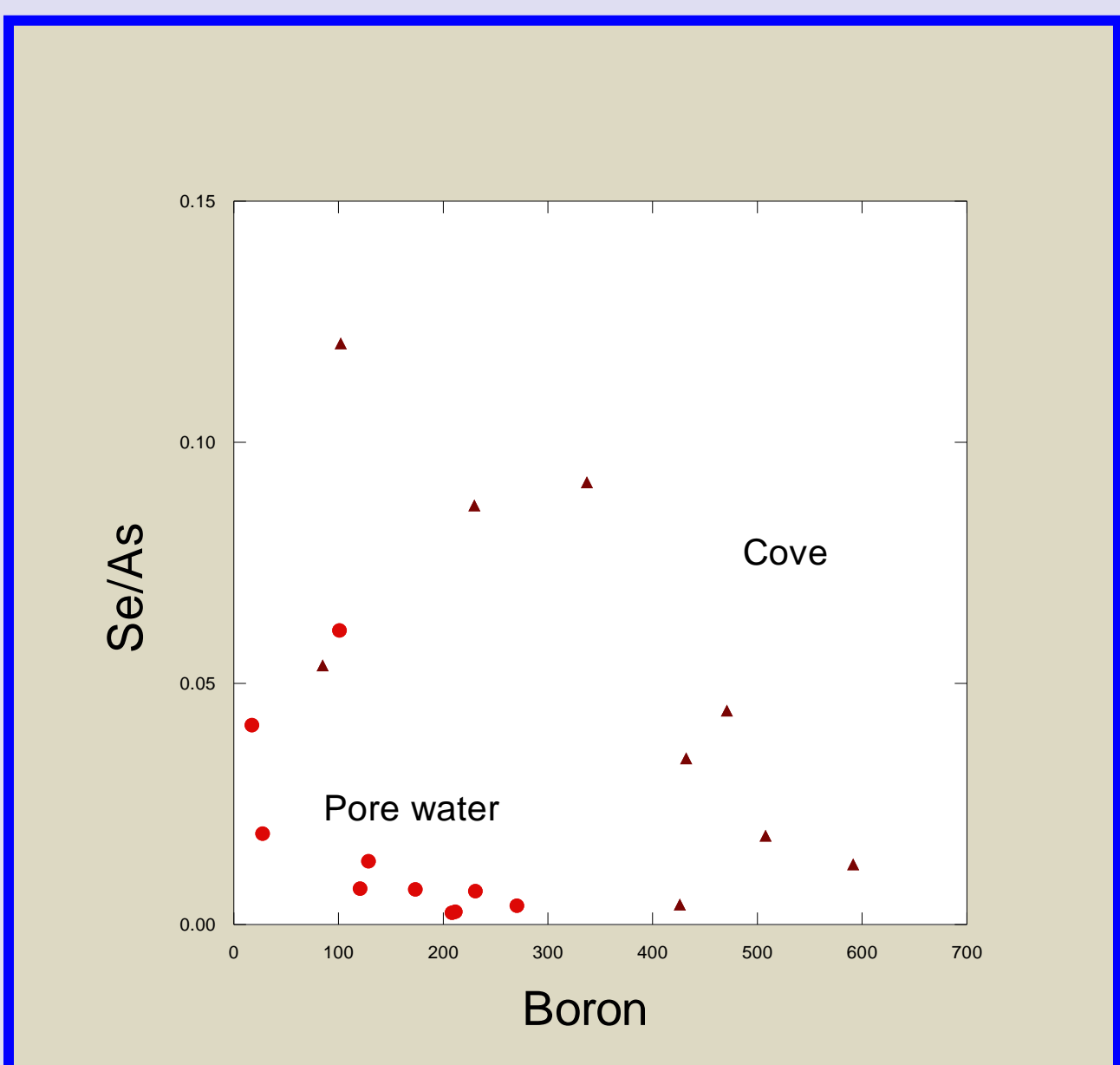
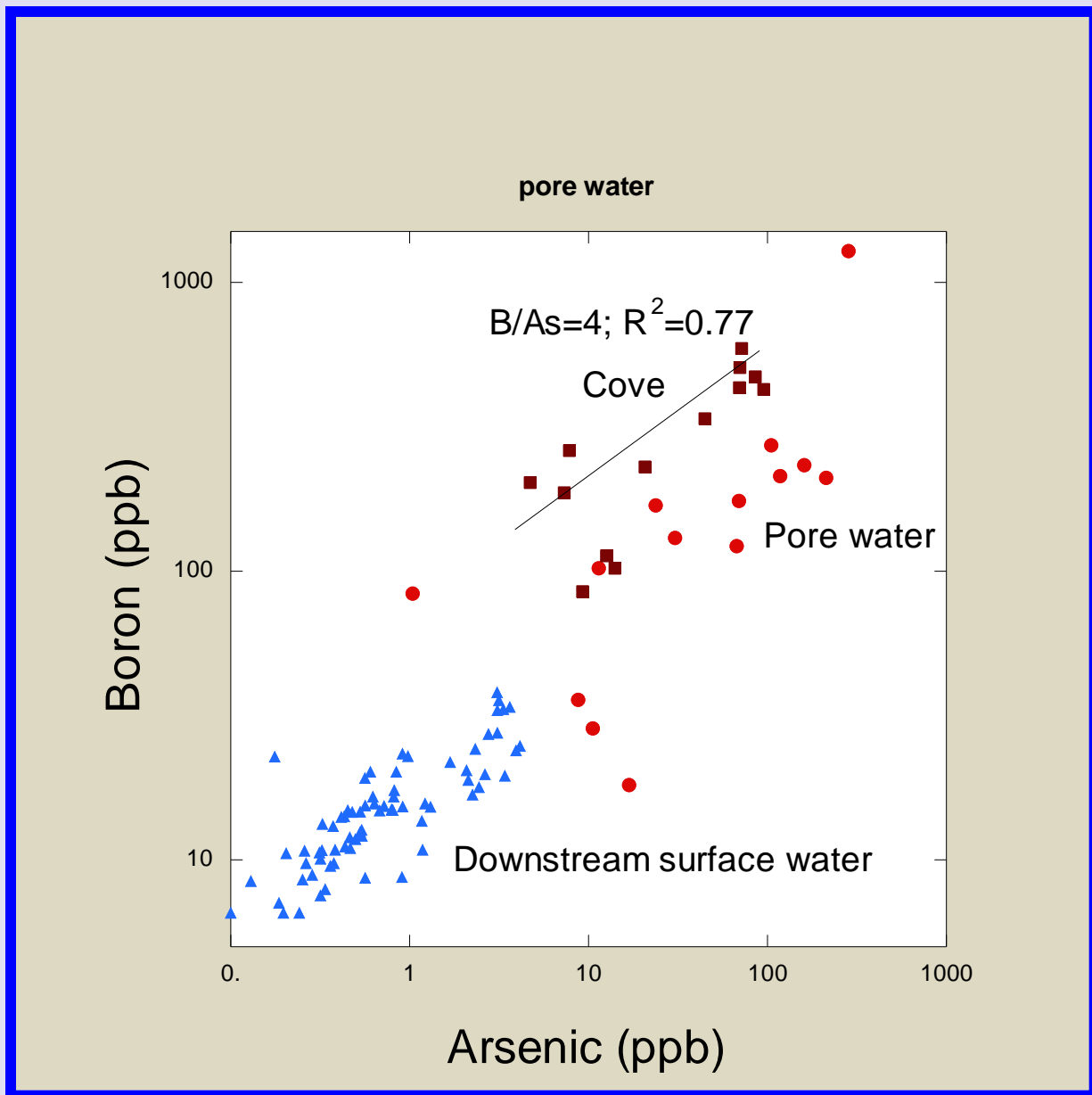


Figure 2: Concentrations of selenium, boron, and arsenic (ppb) in river and pore water as a function of distance from the spill as measured in different time. The concentration of these elements was significantly higher in the pore water as compared to the river water. The highest levels of these contaminants occurred at both pore water and surface water downstream to the spill (~ERM 2.5). Another spike in their concentrations is associated with TVA plant effluent discharge (~CRM 2.5).

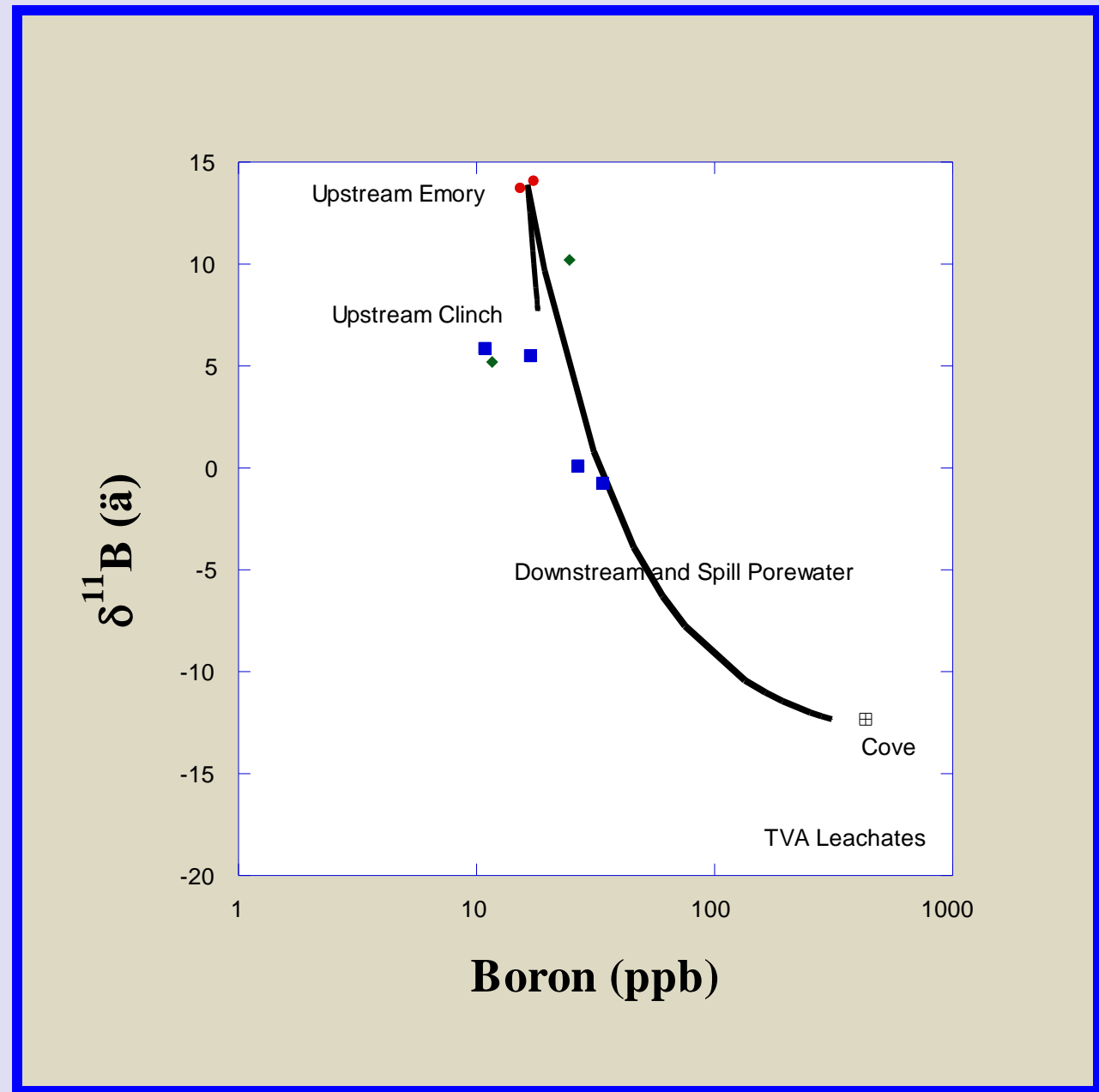


Figures 3, 4, and 5: Figure 3- Relationships between boron and arsenic show that Cove water has higher B/As ratio relative to pore water, but the downstream river surface water mimics the composition of pore water, indicating that the contaminants occurrence in surface water originated from underlying ash leaching to pore water. Figure 4 shows that Cove water has relatively high Se/As ratios relative to pore water. This suggests that under pore water conditions, selenium leaching from the ash is reduced. Figure 5 shows inverse correlation between B/As ratios and  $\delta^{11}\text{B}$  values in downstream pore water relative to the Cove water. This relationship suggests an uptake of boron, probably by adsorption that is associated with isotope fractionation and a slight increase of  $\delta^{11}\text{B}$ . In spite of this modification, the boron isotope composition of the pore water is significantly different from meteoric boron or upstream river and pore water.

## Results:

Three distinctive patterns were revealed:

- (1)surface waters in areas of restricted water exchange (the “Cove”/East Embayment) show high LCACs levels (e.g., As: 9- 95  $\mu\text{g/L}$ ). Removal of ash from this area and diversion of surface water has led to a reduction of the LCAC’s concentrations with time (Figure 3).
- (2) downstream Emory and Clinch Rivers show low LCACs concentrations below the EPA maximum contaminant level (As=10  $\mu\text{g/L}$ ) and Tennessee Fish and Aquatic Life Criterion for Continuous Arsenic Concentration (As= 150  $\mu\text{g/L}$ ) thresholds, but with levels (e.g., As ~4  $\mu\text{g/L}$ ) above the baseline of the upstream rivers (Figure 3 and 4).
- (3) pore water extracted from bottom sediments of the downstream Emory and Clinch rivers with significantly high LCACs levels (e.g., As 9-285  $\mu\text{g/L}$ ) (Figure 4). We identified two “hot spots” of high LCACs levels in pore waters: (1) at ERM 2 derived from massive ash accumulation in sediments; and (2) at CRM 2.5 area that is associated with discharge of TVA plant effluents.



Figures 6: The  $\delta^{11}\text{B}$  values measured for the cove and TVA ash leachates are significantly different from what is found in the upstream Emory and Clinch Rivers. The downstream river water and porewater reflect a mixing of the background  $\delta^{11}\text{B}$  values and the signal from the coal ash.

## Conclusions:

We show that the spilled TVA ash can affect surface water and pore water under conditions of high solid (ash)/water ratios. We show that while significant dilution reduces the LCACs’ impact in the Emory and Clinch Rivers, leaching continues to occur at the bottom sediments and mobilizes LCACs to the underlying pore water. It seems that the trace levels of these contaminants in the river are derived from the pore water. In addition we show that boron is a sensitive indicator for contaminants’ leaching from CCPs. We found high boron content up to 1276  $\mu\text{g/L}$  in pore water, which is significantly higher relative to the upstream river water (6 to 9  $\mu\text{g/L}$ ). The high correlation between boron and arsenic clearly indicates that boron can be used as a sensitive proxy for detection of CCPs’ contaminants in aquatic systems. The boron isotope composition of CCPs’ leachates measured in both leaching experiments and in surface waters at areas of limited water exchange is significantly different from that of upstream Emory River. We therefore use the boron isotope data as additional constraints for quantifying the relative contribution of LCACs in the environment.

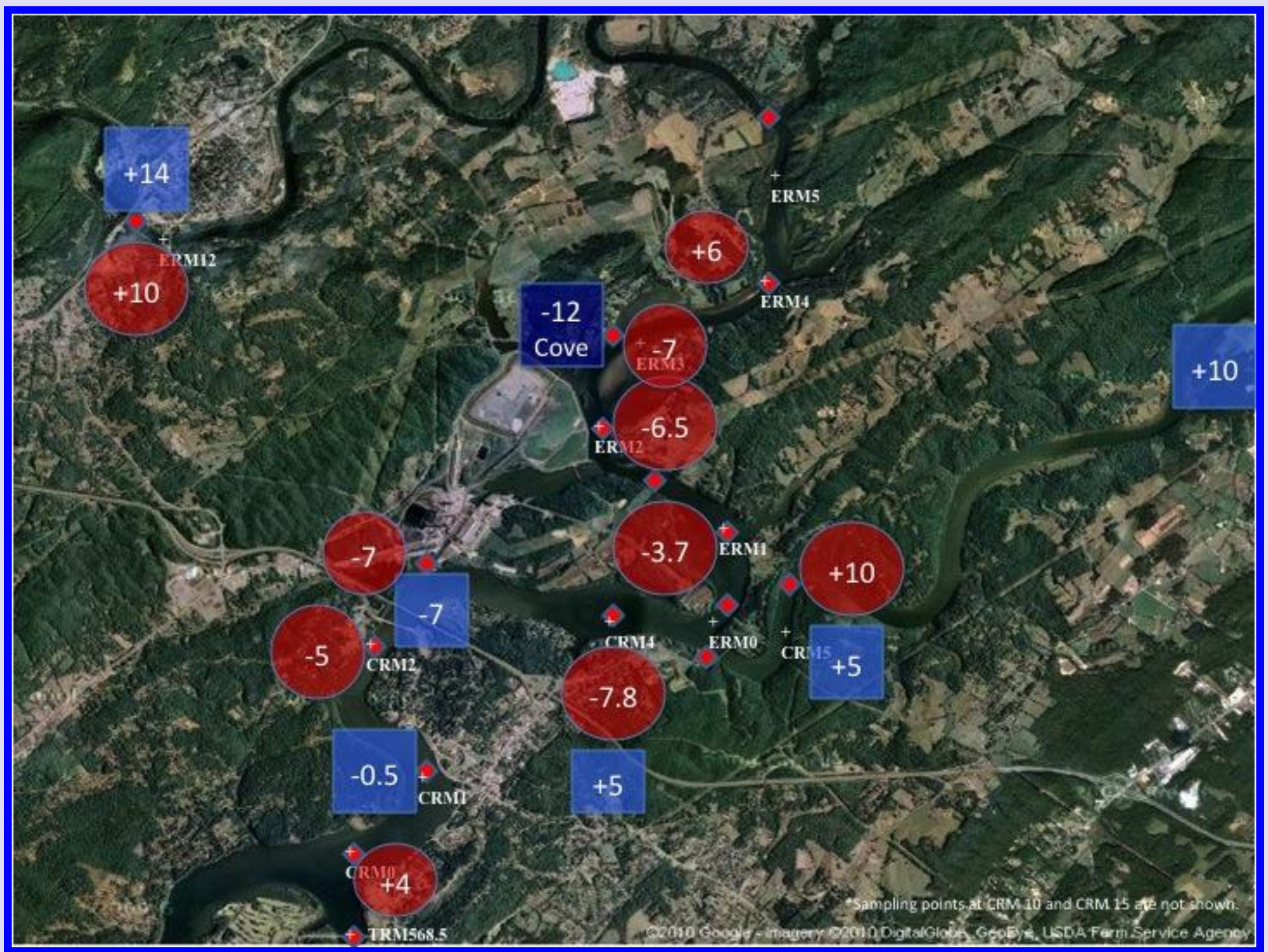


Figure 7: Map of spill region and  $\delta^{11}\text{B}$  values measured in river water (lt. blue squares), the cove (dk. blue square), and porewater (red circles).

## References:

•Ruhl, L., Vengosh, A., Dwyer, G.S., Hsu-Kim, H., Deonarine, A., Bergin, M., and Kravchenko, J. (2009) Survey of the Potential Environmental and Health Impacts in the Immediate Aftermath of the Coal Ash Spill in Kingston, Tennessee. *Env. Sci& Technol.*, 43, 6326–6333.

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